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Type of Organization: College or University

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Project Title: Enhanced Wet Air Oxidation of PCB Contaminated Sediments

Project Category: Contaminated Sediments

Rank by Organization (if applicable):   0

Total Funding Requested ($):   156,096   **Project Duration:**   2   Years

Abstract:

The presence of sediments contaminated by polychlorinated biphenyls (PCBs) is a major problem in the Great Lakes basin. Although landfilling and incineration are approved methods for disposing contaminated sediments, there is widespread public opposition to both of these approaches. Moreover, incineration of sediments contaminated with PCBs can be very costly.

Wet air oxidation is a commercial process used to remediate aqueous waste streams containing organic solutes and to regenerate powdered activated carbon. In a bench scale treatability study conducted by US Filter-Zimpro under guidance from the U.S. Environmental Protection Agency, wet air oxidation was evaluated as a potential method for treating contaminated sediment from the Grand Calumet River. From data generated in this study, EPA personnel concluded that wet air oxidation effectively destroys PAHs but does not appreciably destroy PCBs.

The goal of the proposed project is to enhance the degradation of PCBs adsorbed on sediments through the use of modifications to the conventional wet air oxidation process. Two methods of rate enhancement, addition of hydrogen peroxide and addition of an easily oxidized compound (phenol), will be explored. Addition of either of these compounds following an initial period of conventional wet air oxidation will accelerate the destruction of the remaining PCBs by producing highly active radical species. In preliminary bench-scale studies, the addition of hydrogen peroxide during wet air oxidation of Hudson River sediments significantly increased the rates of oxidation of PCBs. In the proposed study, enhanced wet air oxidation will be evaluated as a method of treating dredged sediments from the Great Lakes basin. Experiments will be performed to determine the optimal temperatures and addition rates of hydrogen peroxide or phenol required to achieve complete destruction of the PCBs. Using these data, the economic feasibility of the process will be analyzed.

Geographic Areas Affected by the Project

States: **Lakes:**

☒ Illinois   ☒ New York   ☐ Superior   ☐ Erie

☒ Indiana   ☒ Pennsylvania   ☐ Huron   ☐ Ontario

☒ Michigan   ☒ Wisconsin   ☐ Michigan   ☒ All Lakes

☒ Minnesota   ☒ Ohio

Geographic Initiatives:

☐ Greater Chicago   ☐ NE Ohio   ☐ NW Indiana   ☐ SE Michigan   ☐ Lake St. Clair

Primary Affected Area of Concern: All AOCs

Other Affected Areas of Concern:

For Habitat Projects Only:

Primary Affected Biodiversity Investment Area:

Other Affected Biodiversity Investment Areas:

Problem Statement:

The sediments in many Areas of Concern within the Great Lakes basin are contaminated with PCBs. Currently, approved methods for treating these sediments involve dredging, de-watering the sediment, and depositing the dry sediment in an approved chemical waste landfill or incinerating the sediment. Although extremely effective for destroying all organic contaminants, incineration of PCB-contaminated sediment is extremely expensive. Also, both of these approved methods have generated strong public opposition. Therefore, investigation of alternative technologies for sediment remediation is warranted.

Wet air oxidation is an extremely attractive method for remediating sediments contaminated with organic compounds. Conventional wet air oxidation utilizes air or oxygen in conjunction with elevated temperatures (150-300oC) and pressures (300-3000psi) to oxidize moderately to highly contaminated waste streams. Fairly simple modifications to commercially available wet air oxidation systems would allow for the treatment of dredged sediments with minimal initial processing of the sediment. Commercially available wet air oxidation systems can process slurries of fine solids with loadings in excess of 10% (w/w). Moreover, moderately sized wet air oxidation units can be skid-mounted and transported to the dredging site, thereby minimizing the transport of dredged sediments. However, as determined in several studies, PCBs are not effectively degraded by conventional wet air oxidation.

The proposed project will investigate modifications to conventional wet air oxidation that will improve the efficiency of PCB degradation. Specifically, two methods of rate enhancement, addition of hydrogen peroxide and addition of an easily degradable organic compound (phenol) will be explored. Addition of either of these compounds following an initial period of conventional wet air oxidation will accelerate the destruction of the remaining PCBs by producing highly active radical species. The overall objective of this study is to determine optimal conditions for enhanced wet air oxidation of contaminated sediments and evaluate the economic feasibility of this process using rate data collected in experiments.

Proposed Work Outcome:

The feasibility of using enhanced wet air oxidation to remediate sediments will be evaluated by completing five primary tasks.
1. Construct the wet air oxidation reactor system and obtain contaminated sediment.
2. Determine baseline kinetic data for conventional wet air oxidation of sediments.
3. Evaluate the addition of hydrogen peroxide during wet air oxidation of sediments.
4. Evaluate the addition of phenol during wet air oxidation of sediments.

5. Evaluate the economic feasibility of the enhanced wet air oxidation processes.

Task 1 Construct the wet air oxidation reactor system and obtain contaminated sediment.
A one-liter high-pressure stirred reactor with connections for pressurization with oxygen, pressure measurement, over-pressure protection, depressurization, addition of chemicals, internal cooling, and temperature control will be purchased from one of several vendors (Parr Scientific, Pressure Products Industries, Autoclave Engineers, etc.). Sediment contaminated with PCBs will be obtained from one or more sites in the Great Lakes basin that have or are currently conducting dredging operations.

Task 2 Determine baseline kinetic data for conventional wet air oxidation of sediments.
Note: All kinetic studies will be conducted using a 10% (w/w) sediment in water slurry. Effluent sediments will be analyzed for organic matter and PCB concentrations. Effluent water (filtrate) will be analyzed for organic carbon, PCB, and selected metals concentrations. Volatile organic compounds in the reactor headspace will be trapped and analyzed for PCBs. All sediment analyses will be conducted using standard EPA procedures (e.g.,EPA SW-846 Method 8082) for PCB extraction, sample cleanup, and congener specific GC analysis. A certified reference material sediment (National Institute of Standards and Technology: Standard Reference Material 1939a - PCBs in River Sediment) will be used to periodically evaluate the accuracy of experimental protocols for extraction, cleanup, and analysis.

Studies by other research groups indicate that in wet air oxidation systems the rate at which oxygen can be supplied may limit the rate of oxidation. For batch reactor operation, the rate at which oxygen can be supplied to the reacting solution from the headspace is a function of the stirring speed. The role of oxygen mass transport processes on the overall reaction rates in our system will be assessed by measuring the destruction efficiencies for sediment organic matter and PCBs at several stirring rates. From this data, the minimum stirring speed required to ensure the absence of oxygen mass transport limitations will be determined.

Second, destruction efficiencies for sediment organic matter and PCBs will be determined at 250oC and reaction times of 0.5, 1.0, 1.5, and 2 hours. This kinetic data will be used as a baseline for comparison of the enhanced wet air oxidation treatments.

Task 3 Evaluate the addition of hydrogen peroxide during wet air oxidation of sediments.
An aqueous solution of hydrogen peroxide will be continuously fed to the reactor following an initial period of conventional wet air oxidation at 250oC. At elevated temperatures, hydrogen peroxide decomposes to produce hydroxyl radicals, which are known to effectively oxidize PCBs. The duration of the initial period of conventional wet air oxidation will be determined using data obtained in performing task 2. This initial period of conventional wet air oxidation will result in the oxidation of a substantial portion of the generic sediment organic matter, which would have otherwise competed with the PCBs for reaction with hydroxyl radicals. The temperature of the reactor and rate of addition of hydrogen peroxide will be systematically varied in order to determine optimal operating conditions for complete (>99.9%) destruction of PCBs.

Task 4 Evaluate the addition of phenol during wet air oxidation of sediments.
Experiments performed in task 3 will be repeated using an aqueous solution of phenol in place of hydrogen peroxide. The rapid degradation of phenol by wet air oxidation will result in the production of active radical species (hydroxyl and alkoxyl radicals) that are known to effectively oxidize PCBs. This "kinetic coupling" phenomena has been observed in the wet air oxidation of m-xylene in the presence of phenol. The rate of oxidation of m-xylene in the presence of an equimolar concentration of phenol was more than one order of magnitude greater than that for m-xylene alone. The temperature of the reactor and rate of addition of phenol will be systematically varied in order to determine optimal operating conditions for complete (>99.9%) destruction of PCBs.

Task 5 Evaluate the economic feasibility of the enhanced wet air oxidation processes.
The kinetic data generated in tasks 3 and 4 and cost estimate data provided by US Filter-Zimpro, a manufacturer of wet air oxidation systems, will be utilized to estimate capital and operating costs for treating dredged sediments using enhanced wet air oxidation. These estimates will be compared to cost estimates for incineration and landfilling of PCB-contaminated sediments.

Project Milestones:	**Dates:**
Project Start	09/2000
Task 1 Completed	12/2000
Task 2 Completed	04/2001
Task 3 Completed	08/2001
Task 4 Completed	12/2001
Task 5 Completed	03/2002
Draft Report and Papers	06/2002
Final Report and Papers Submitted	08/2002

☐   Project Addresses Environmental Justice

If So, Description of How:

☒   Project Addresses Education/Outreach

If So, Description of How:

Money allocated for this project will be utilized to fund a graduate student and two undergraduate students for two years. This time period is sufficient for the graduate student to complete a program leading to a Masters degree in chemical or environmental engineering. The undergraduate students will work both with the graduate student and on independent but related projects. The two year time period will allow for the completion of a substantial undergraduate research project by each student. In addition, conference presentations and peer-reviewed publications will be used to disseminate the results of this project.

Project Budget:

	Federal Share Requested ($)	Applicant's Share ($)
Personnel:	56,800	0
Fringe:	6,840	0
Travel:	2,000	0
Equipment:	30,000	15,000
Supplies:	12,000	0
Contracts:	1,000	0
Construction:	0	0
Other:	16,000	0
Total Direct Costs:	124,640	15,000
Indirect Costs:	31,456	0
Total:	156,096	15,000
Projected Income:	0	0

Funding by Other Organizations (Names, Amounts, Description of Commitments):

Approximately 10% of the total project costs will be provided in cash by funding available to my research group from the Department of Chemical Engineering and the College of Engineering at Montana State University.

Description of Collaboration/Community Based Support: